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A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS

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By

HENRY L. McMURRY

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The Long Wave-Length Spectra of Aldehydes and Ketones

Part I. Saturated Aldehydes and Ketones

HENRY L. MCMURRY

Ryerson Physical Laboratory, University of Chicago, Chicago, Illinois

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Intensity calculations are used to help in deciding which of two theoretically predicted transitions should be identified with the weak longest wave-length absorption

characteristic of the unconjugated $\text{C}=\text{O}$ group. In terms

of the localized *LCAO MO* and the *AO* approximations used, one of these transitions is forbidden while the calculated intensity for the other, allowed, transition is much too large to be compatible with the low intensities observed for the absorption. The observed absorption should, therefore, be ascribed to the forbidden transition. The *Q* and *S* integrals needed for the calculations, involving *AO*'s of the C and O atoms, are tabulated. The intensity for the allowed transition, when expressed using semi-localized *LCAO MO*'s depends somewhat on the nature of

the atoms attached to the $\text{C}=\text{O}$ group. The absorption regions appearing at shorter wave-lengths in ketones and aldehydes are discussed. It is concluded that the $\lambda 1900$ region in ketones is characteristic of the $\text{C}=\text{O}$ group and probably is due either to a Rydberg transition or most likely to the allowed transition for which intensity calculations have been made. If the latter is true the upper level of the $\lambda 1900$ absorption could be largely responsible for the perturbations which cause the appearance of the long wave-length forbidden transition. It is shown that the long wave-

length absorptions from the $\text{C}=\text{S}$ group can be explained

in the same manner as those for the $\text{C}=\text{O}$ group.

I. INTRODUCTION

WHENEVER the carbonyl $\left(\text{C}=\text{O} \right)$ group is present in a molecule a weak absorption region appears at relatively long wave-lengths.¹⁻⁵

¹ Cf. E. Eastwood and C. P. Snow, *Proc. Roy. Soc. A* **149**, 434 (1935).

In saturated aldehydes and ketones (molecules of the type $\text{RR}'\text{CO}$, where R and R' are alkyl

² G. Scheibe and W. Frömel, *Eucken-Wolf Hand- und Jahrbuch der chem. Physik* **9**, Part IV (1936); especially p. 164 on.

³ F. O. Rice, *Proc. Roy. Soc. A* **91**, 76 (1914-1915); pure liquid ketones.

⁴ J. Bielecki and V. Henri, *Ber. d. D. Chem. Ges.* **46**, 3627 (1913); aldehydes and ketones in alcohol solution.

⁵ *Int. Crit. Tab. Vol. 5*; Landolt-Börnstein, *Physikalisch-Chemische Tabellen*.

groups or hydrogen atoms) this absorption always appears somewhere near $\lambda 2900$ and possesses a low intensity which is of the same order of magnitude for all these molecules. In conjugated aldehydes and ketones, where a C=O group is conjugated with a C=C group or with another C=O group, this weak absorption is shifted toward longer wave-lengths.^{2, 5}

The regularity with which this absorption appears in molecules containing the C=O group shows definitely that the absorption arises from this group, while the similarity of its intensity in all these molecules strongly suggests that the transition is essentially the same regardless of the molecule for which it is observed.

In formaldehyde (H_2CO) this absorption consists of a series of very sharp bands. The rotational analysis for some of these bands has been given by Dieke and Kistiakowsky.⁶ Using this analysis, Mulliken⁷ showed that, among all the possible excited states possessing the proper symmetry characteristics to explain the observed band structures, only two appeared to merit consideration. The transition to one of these states involves excitation of an electron from a wave function in the molecular plane and having a node through the C—O line to a wave function which is perpendicular to this plane and also has a node through the C—O line. Apparently the wave function from which this excitation comes is largely localized on the oxygen atom and its electron is nearly nonbonding. The other transition involves excitation of this same nonbonding oxygen electron to a wave function concentrated along the C—O direction.

The first of these two transitions is forbidden by the electronic selection rules but may still be capable of producing the observed absorption because perturbations of the electronic wave functions by molecular vibrations can remove the "forbiddenness" of the transition.⁸ The second transition is an allowed transition which, on examination, is seen to be essentially of the

perpendicular $N \rightarrow Q$ type recently discussed by Mulliken,^{9, 10} except that here nondegenerate states are involved.

In other molecules containing the C=O group transitions analogous to these must occur. In most of these molecules the symmetry of formaldehyde (C_{2v}) is only approximately preserved for the C=O group and its attached atoms, and the transition which is forbidden in H_2CO becomes formally allowed. The intensity for this transition may, therefore, be expected to increase in the more complex molecules where the symmetry is the lowest and where changes in the electronic-vibrational interactions⁸ may also alter this intensity. However, both transitions are expected to retain their distinguishing features even in the more complicated molecules, and for this reason they will be respectively referred to hereafter as the *allowed* and the *forbidden* transitions.

Several lines of evidence favor the assignment of the *forbidden* transition as explaining the long wave-length absorption in aldehydes and ketones. Gradstein¹¹ has shown that the vibrational structure of the long wave-length fluorescence and absorption bands in H_2CO can be analyzed best if they are assumed to come from a forbidden transition. According to Scheibe and Frömel the intensity for this absorption in other aldehydes and ketones increases somewhat with growing complexity of the constituents attached

to the C=O group.¹² This behavior might be

expected for the forbidden transition in these molecules. McMurry and Mulliken¹³ have pointed out that the calculated intensity for the allowed transition appears to be too high to explain the observed long wave-length absorption in aldehydes and ketones. Furthermore, the shift of the absorption toward still longer wave-lengths upon conjugation of a C=O group with C=C or

⁹ R. S. Mulliken, J. Chem. Phys. **8**, 234 (1940).

¹⁰ R. S. Mulliken, J. Chem. Phys. **8**, 382 (1940).

¹¹ S. Gradstein, Zeits. f. physik. Chemie **B22**, 384 (1933).

¹² See reference 2, p. 169. This effect is noted particularly

for molecules in which the C=O group is conjugated with C=C or other C=O groups but is said to be present in the saturated molecules also.

¹³ H. L. McMurry and R. S. Mulliken, Proc. Nat. Acad. Sci. **26**, 312 (1940).

⁶ G. H. Dieke and G. B. Kistiakowsky, Proc. Nat. Acad. Sci. **18**, 367 (1932); Phys. Rev. **45**, 4 (1934).

⁷ R. S. Mulliken, J. Chem. Phys. **3**, 564 (1935).

⁸ This type of transition has been discussed by G. Herzberg and E. Teller (Zeits. f. physik. Chemie **B21**, 410 (1933)). The weak long wave-length absorption near $\lambda 2600$ in benzene is an example of such a transition (H. Sponer, G. Nordheim, A. L. Sklar and E. Teller, J. Chem. Phys. **7**, 207 (1939)).

other C=O groups was shown to be in agreement with the nature of the forbidden transition. The present work gives details of the intensity calculations and the conclusions to be derived from them.

II. THE USE OF INTENSITY CALCULATIONS IN IDENTIFYING ELECTRONIC TRANSITIONS

A. The validity of the calculations

Mulliken has shown that for many transitions where the type of excited state is known, the observed absorption intensity is of the same order of magnitude as that calculated quantum-mechanically, using approximate molecular wave functions.^{9,10,14-16} These comparisons have been made for several molecules where transitions of the perpendicular $N \rightarrow Q$ type, analogous to that for the allowed transition considered here for the carbonyl group, are known.^{9,10} Considering the nature of the calculations, the agreement between calculated and observed intensities for most of these molecules is good and the ratio of the calculated to the observed intensity is roughly the same for all the molecules. There are some exceptions for molecules with heavy nuclei like I_2 , but these appear to be connected with the very strong spin-orbit coupling which occurs in these molecules. This condition cannot be present in aldehydes and ketones.

These results indicate that the calculated intensity for the allowed transition in aldehydes and ketones should, after multiplication by a suitable correction factor, be close to the actual intensity. A calibration factor can be obtained from the ratio of the observed to calculated intensities for the known $N \rightarrow Q$ transitions in other molecules.^{9,10} Intensities obtained by so multiplying the calculated intensity by a correction factor will hereafter be referred to as *predicted* intensities.

B. Application

The intensity observed for any absorption region in a molecule can be compared with the predicted intensities for the theoretically expected transitions most capable of explaining the

absorption. In seeking possible assignments for the absorption, those transitions for which the predicted intensities differ widely from the observed may be excluded.

In explaining the longest wave-length absorption in aldehydes and ketones there is a choice between the "allowed" and the "forbidden" transitions. Since the intensity can be predicted only for the allowed transition, it alone can be compared with that observed for the longest wave-length absorption. If there should be agreement, this absorption could safely be ascribed to the allowed transition. The forbidden transition would then be expected to occur nearby, but probably with a much lower intensity.¹⁷ However, if the predicted intensity should be much larger than the observed (this is actually the case), the long wave-length absorption would be assigned to the forbidden transition and the allowed transition would be sought at shorter wave-lengths.

C. Methods of calculation

Comparisons between observed and calculated intensities may be made either through the use of the dipole strength, Q^2 , or the f value for the transition.¹⁸ These quantities are related approximately as follows.⁹

$$f = 1.09 \times 10^{11} Q^2 \nu, \quad (1)$$

where ν is the position of the center of the absorption band in cm^{-1} .

A theoretical value of Q can be obtained by evaluating the electric moment integral (reference 18, Eq. (4)) using approximate wave functions for the states involved in the transition. With the aid of Eq. (1) this Q may be compared with the experimentally determined f obtained by integrating the observed absorption coefficient across the band (Eqs. (19) and (3) of reference 18).

In the present work Q will be calculated for the allowed transition in H_2CO , using both the

¹⁷ Conceivably the intensity of the forbidden and allowed transitions might be about the same. However, this would require two absorptions of at least noticeable intensity fairly close together. This apparently is not observed for these molecules.

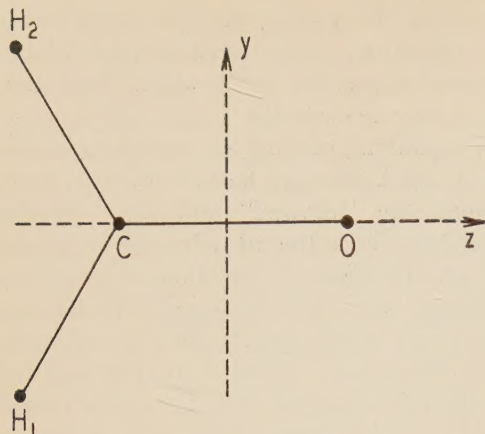
¹⁸ Cf. R. S. Mulliken, J. Chem. Phys. 7, 14 (1939); also references 9, 10, 14-16.

¹⁹ A factor G' , corresponding to the number of degenerate wave functions appearing in the excited state, has been omitted in Eq. (1). Its value in the present case is one.

¹⁴ R. S. Mulliken, J. Chem. Phys. 7, 20 (1939).

¹⁵ R. S. Mulliken, J. Chem. Phys. 7, 121 (1939).

¹⁶ (a) R. S. Mulliken, J. Chem. Phys. 7, 364 (1939); (b) *ibid.* 7, 570 (1939).

FIG. 1. Axes for H_2CO .

atomic orbital (AO) and the localized molecular orbital (MO) approximations to the molecular wave functions. The theoretical intensity obtained for H_2CO will be shown to apply without appreciable change to other aldehydes and ketones, and can therefore be compared with the experimentally determined intensity for these molecules.

For any approximation, it is convenient first to write down electron configurations for each of the electronic states involved in a transition; next to write out the corresponding wave functions; finally, to substitute in the integral for Q .

III. INTENSITY CALCULATIONS FOR THE ALLOWED TRANSITION IN H_2CO

A. Localized MO configurations for H_2CO

Usually calculations can be made only in terms of MO's approximated by LCAO forms (linear combination of the outer shell AO's of the atoms involved). In this section calculations will be made in terms of *localized* LCAO MO's.²⁰ The intensity predicted in terms of *nonlocalized* LCAO MO's will be discussed qualitatively in a later section (III H).

In constructing the MO's for H_2CO the $2p$ AO's of the carbon and oxygen atoms will be taken with their positive parts directed along the positive x , y , or z directions (cf. Fig. 1), except for $(2p_z)_O$ which will be taken with its

positive part toward the carbon atom. For simplicity the symbols s_C , x_C , y_O , z_O and so on, will be used to denote the AO's $(2s)_C$, $(2p_x)_C$, $(2p_y)_O$, $(2p_z)_O$ and so on.

In H_2CO it is known that the bonds extending from the carbon atom lie in the molecular plane and are about 120° apart.²¹ Carbon orbitals suitable for these bonds may be approximated by forming three mutually orthogonal linear combinations of y_C , z_C and s_C AO's.²² These mixed AO's will be denoted by t_1 , t_2 and t_3 . The AO's t_1 and t_2 are used with the hydrogen $1s$ AO's s_1 and s_2 to form localized bonding MO's, while the t_3 and z_O AO's are used to form one of the two C—O bonding MO's. Suitable forms for the t AO's of carbon have been described by Pauling; in the present calculations "trigonal" AO's have been employed.²² The second of the two C—O bonding MO's is formed using the x_C and x_O AO's.

The electron configurations for the normal state and for the two excited states (which may be called 1E and 1Z) involved in the forbidden and allowed transitions, respectively, are written as follows:²³

$$\begin{array}{ll} ^1N \cdots (s_1 t_1)^2 (s_2 t_2)^2 (t_3 z_O)^2 (x_C x_O)^2 (y_O)^2, & ^1A_1 \\ ^{3,1}E \cdots \cdots \cdots \cdots \cdots (y_O)(x_C \bar{x}_O), & ^{3,1}A_2 \\ ^{3,1}Z \cdots \cdots \cdots \cdots \cdots (y_O)(t_3 \bar{z}_O), & ^{3,1}B_2. \end{array} \quad (2)$$

Here any symbol such as $(s_1 t_1)$ indicates an electron in a localized MO built up from the AO's, s_1 and t_1 .²⁰ The bars used in the excited configurations indicate antibonding MO's. In this approximation the $2p_y$ electrons are assumed to be localized entirely on the oxygen atom, and

²¹ D. P. Stevenson, J. E. LuValle and V. Shomaker, J. Am. Chem. Soc. **61**, 2508 (1939): electron diffraction of H_2CO .

²² Cf. L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, 1939), pp. 88 and 89, footnotes. The pure "trigonal" functions are as follows:

$$\begin{aligned} t_1 &= -s_C/3^{1/2} + y_C/2^{1/2} - z_C/6^{1/2} \\ t_2 &= -s_C/3^{1/2} - y_C/2^{1/2} - z_C/6^{1/2} \\ t_3 &= s_C/3^{1/2} + z_C/2^{1/2} \end{aligned}$$

Other somewhat more general mixtures of s_C , y_C and z_C are also given by Pauling and would be appropriate here. Calculations made in terms of these give results differing but little from those obtained with the trigonal forms used above.

²³ The species symbols 1A_1 , 3,1A_2 , 3,1B_2 in Eq. (2) apply strictly only to molecules having C_{2v} symmetry. The symbols 1N , 1E , and 1Z may be used to refer to the states of aldehydes and ketones where the C_{2v} symmetry is no longer present. (See reference 34 for a discussion of the use of symmetry properties in describing molecular wave functions.)

²⁰ Cf. F. Hund, Zeits. f. Physik, **73**, 1, 565 (1931-32). Also see R. S. Mulliken, J. Chem. Phys. **3**, 375 (1935) for an outline of the method of molecular orbitals.

to be nonbonding. For this the brief symbol y_0 is used in (2). The triplet states indicated in (2) should exist as low energy states but transitions to them are probably so exceedingly weak that they have escaped observation.

B. AO configurations for H_2CO

The AO wave functions for the normal and excited states of H_2CO can be approximated by linear combinations of wave functions corresponding to both polar and nonpolar charge distributions in the $C=O$ part of the molecule. Several configurations are, therefore, needed to describe a single electronic state.²⁴ Those which contribute most to the normal and excited states N and Z of H_2CO are given in Eq. (3). The description of the E state is omitted since it is not involved in the present calculations:

$${}^1N: \left\{ \begin{array}{ll} (s_1 \cdot t_1)(s_2 \cdot t_2)(t_3 \cdot z_0)(x_C \cdot x_O)(y_O \cdot y_O), & \text{I} \\ \cdots \cdots (z_O \cdot z_O) \cdots \cdots & \text{II} \\ \cdots \cdots (t_3 \cdot z_0)(x_O \cdot x_O) \cdots & \text{III} \end{array} \right\} A_1 \quad (3)$$

$${}^3Z: \left\{ \begin{array}{ll} (s_1 \cdot t_1)(s_2 \cdot t_2)(t_3 \cdot z_0)(x_C \cdot x_O)(z_O \cdot y_O), & \text{IV} \\ \cdots \cdots \cdots \cdots (y_O \cdot t_3), & \text{V} \\ \cdots \cdots \cdots (x_C \cdot x_C)(z_O \cdot y_O), & \text{VI} \end{array} \right\} {}^3B_2.$$

Here any symbol such as $(s_1 \cdot t_1)$ represents two electrons in two AO 's (in this case s_1 and t_1), the electrons being paired with opposite spins. The numbers I, II $\cdots$ VI will be used later in designating the wave functions corresponding to the configurations bearing these numbers.

In Eq. (3) the normal state configurations II and III correspond to C^+O^- polarity while in the excited state Z , configurations V and VI correspond to C^-O^+ polarity. Polar configurations other than these are expected to give only small contributions and have been omitted.

C. Wave functions for H_2CO

For making intensity calculations, abbreviated wave functions can be used which include only those electrons affected by the transition.²⁵ In the MO treatment only the electrons in MO 's from or to which excitation takes place need be con-

sidered. In the AO treatment all pairs of electrons which are not identical in the initial and final wave functions of the transition must be included.

In the present case these rules make possible calculations with two- or six-electron wave functions, depending on whether the MO or the AO wave functions are employed. The MO and AO wave functions for the 1N and 1Z states described in (2) and (3) may be expressed as follows:

$$MO: \psi({}^1N) = y_O(1)y_O(2) \\ \psi({}^1Z) = 2^{-1/2}[y_O(1)t_3z_O(2) + t_3z_O(1)y_O(2)], \quad (4)$$

$$AO: \psi({}^1N) = (a\psi_I + 2^{1/2}b\psi_{II} + 2^{1/2}c\psi_{III})/2 \times (6!)^{1/2} \\ \psi({}^1Z) = (a'\psi_{IV} - b'\psi_V + 2^{1/2}c'\psi_{VI})/2 \times (6!)^{1/2}. \quad (5)$$

Here the wave functions corresponding to the configurations I, II $\cdots$ VI of (3) are denoted respectively by $\psi_I, \psi_{II} \cdots \psi_{VI}$. The following normalizing relations hold for the coefficients appearing in the AO expressions for $\psi({}^1N)$ and $\psi({}^1Z)$ in Eq. (5).²⁶

$$a^2(1+S_\pi^2)(1+S_\sigma^2) + b^2(1+S_\pi^2) + c^2(1+S_\sigma^2) \\ + 2^{1/2}[abS_\sigma(1+S_\pi^2) + acS_\pi(1+S_\sigma^2)] \\ + 2bcS_\sigma S_\pi = 1; \quad (6)$$

$$S_\sigma = \int z_O t_3 dv, \quad S_\pi = \int x_C x_O dv$$

$$a'^2(1-S_\sigma^2)(1+S_\pi^2) + b'^2(1-S_\sigma^2)(1+S_\pi^2) \\ + c'^2(1-S_\sigma^2) + a'b'S_\sigma(1-S_\sigma^2)(1+S_\pi^2) \\ + 2^{1/2}[a'c'S_\pi(1-S_\sigma^2) \\ + b'c'S_\pi S_\sigma(1-S_\sigma^2)] = 1. \quad (7)$$

The wave functions $\psi_I \cdots \psi_{VI}$ of (5) can be expressed as six-electron wave functions analogous to the four-electron wave functions used by Mulliken to describe the N and Q states of the hydrogen halides.¹⁰

D. Intensity calculations for H_2CO

The wave functions given in Eqs. (4) and (5) may be used to evaluate the dipole moment integral.¹⁸ The procedure for doing this has been

²⁶ When an electronic state is described using a combination of ionic and nonpolar AO configurations its wave function approaches that used in the $LCAO$ MO approximation. The signs of the coefficients of the terms in the AO wave function may be determined by expanding the corresponding $LCAO$ MO wave function and comparing the signs of like terms which appear in both approximations. This method has been used here to determine the signs of a, b, c, a', b' , and c' in (5). These coefficients are themselves here taken as positive numbers.

²⁴ Cf. J. H. Van Vleck and A. Sherman, Rev. Mod. Phys. 7, 167 (1937).

²⁵ See reference 9, footnote 18, p. 239, where these simplifications are discussed for the wave functions employed for calculating the $N \rightarrow Q$ intensities in the halogen molecules.

described by Mulliken.⁹ This procedure gives the following expressions using the *MO* and *AO* approximations, respectively:²⁷

$$MO: Q = 2^{\frac{1}{2}} \int (y_0) y(t_3 z_0) dv = 2^{\frac{1}{2}} g Q_{y_0 t_3}, \quad (8)$$

$$AO: Q = Q_{y_0 t_3} \{ [1 + S_{\pi}^2] [2aa'S_{\sigma} + ab'(1 + S_{\sigma}^2) + 2^{\frac{1}{2}}(ba' + bb'S_{\sigma})] + S_{\pi} [2^{\frac{1}{2}}S_{\sigma}(ac' + ca') + 2bc' + 2^{\frac{1}{2}}cb'(1 + S_{\sigma}^2) + 2cc'S_{\sigma}S_{\pi}] \}. \quad (9)$$

Here

$$Q_{y_0 t_3} = \int (y_0) y(t_3) dv. \quad (9a)$$

The coefficients a, b, c, a', b', c' are those appearing in Eq. (5). The letter y in Eqs. (8) and (9a) stands for the coordinate y of a single electron, and originates from $\sum q_i$ in Eq. (4) of reference

18 which here becomes $\sum y_i$, since the transition considered is y -polarized. The symbols y_0 and t_3 refer to *AO*'s already discussed.

A useful estimate for the value of the integral $Q_{y_0 t_3}$ appearing in Eqs. (8) and (9) may be obtained by calculating it in terms of the analytic *AO*'s described by Slater.²⁸ The polarity coefficients g, a and so forth in Eqs. (8) and (9) may be estimated so as to be in harmony with information concerning the electro-negativities of the atoms in the molecule.²⁹ When this is done,

TABLE I. Q and S integrals ($r_{CO} = 1.22A$).

INTEGRAL	VALUE (Q 's IN A)	INTEGRAL	VALUE
$Q_{y_0 z_C}$	0.159	$\int z_0 z_C dv$	0.31
$Q_{y_0 s_C}$	0.137	$\int z_0 t_3 dv$	0.43
$Q_{y_0 t_3}$	0.208	$\int x_C x_O dv$	0.22
$\int z_0 z_C dv$	0.31		

²⁷ These expressions are similar to those obtained by Mulliken for the analogous transitions in the hydrogen halides (reference 10, Eqs. (24) and (34)). In the hydrogen halides the excited states are degenerate. The Q 's for transitions to all of the degenerate states are given by expressions which are obtained in the same way as the Q for the $N \rightarrow Z$ transition discussed here. In the present case the coefficients c and c' appear because the x electrons introduce new terms in the wave functions for the 1N and 1Z states. If these coefficients are put equal to zero, Eq. (9) becomes identical with Eq. (34) of reference 10 when $Q_{\sigma\pi} = 0$ and $c = 0$ in that equation. In the hydrogen halides the coefficient c represents the contribution of the A^-X^+ configuration to the normal state. The analogous contribution is here certainly small, and has been taken to be zero.

²⁸ J. C. Slater, Phys. Rev. **36**, 57 (1930).

²⁹ R. S. Mulliken, J. Chem. Phys. **2**, 782 (1934); **3**, 573 (1935).

theoretical values of the dipole strength or the f value may be obtained for comparison with observed values for the longest wave-length absorption.

E. Intensities for aldehydes and ketones

Since the integrated intensity for the long wave-length absorption is not known for formaldehyde itself, comparison must be made using experimental absorption curves of other aldehydes and ketones either as pure liquids or in solution.^{3-5, 30-32} This is justified because Eqs. (8) and (9) apply equally well to all aldehydes and ketones. This statement is based on the fact that the atoms adjacent to the carbon atom of the

C=O group are probably always in the same

plane with this group and lie in directions from the carbon atom which are close to 120° apart.³³ Thus the carbon *AO*'s used in forming the localized bonds from the carbonyl group are essentially the same for all aldehydes and ketones, and those parts of the wave function describing the two C=O bonds are essentially the same for all these molecules. Since the *AO*'s describing the C=O bonds are the only ones appearing in the expressions for Q (Eqs. (8) and (9)), these equations may be employed in calculating the intensity for this transition re-

gardless of the molecule containing the C=O group.

F. Results

Numerical values for the integrals appearing in Eqs. (8) and (9), calculated using Slater *AO*'s,²⁸ are given in Table I. The integral $Q_{y_0 t_3}$ is composed of two parts, $Q_{y_0 s_C}$ and $Q_{y_0 z_C}$, correspond-

³⁰ G. Scheibe, Ber. d. D. Chem. Ges. **58**, 586 (1925); acetone in hexane, conjugated ketones.

³¹ H. Ley and B. Arends, Zeits. f. physik. Chemie **B12**, 132 (1931); J. Bielecki and V. Henri, Ber. d. D. Chem. Ges. **46**, 3627 (1913); pure acetone.

³² A. Lüthy, Comptes rendus **176**, 1547 (1923); Zeits. f. physik. Chemie **A107**, 285 (1923); acetaldehyde, acrolein and crotonaldehyde in hexane.

³³ Cf. reference 21, also D. P. Stevenson, H. D. Burnham and V. Shomaker, J. Am. Chem. Soc. **61**, 2922 (1939); J. E. LuValle and V. Shomaker, J. Am. Chem. Soc. **61**, 3520 (1939), for information from electron diffraction experiments on several aldehydes and ketones.

TABLE II. Calculated and observed values of Q^2 and f .

	USING Q FROM EQ. (8)	USING Q FROM EQ. (9)*				OBS. VALUES†
		NONPOLAR N AND Z STATES ($b=c=0$; $a=0.90$; $b'=c'=0$; $a'=1.08$)	POLAR N STATE, NON- POLAR Z STATE ($b=c=a/2^{\frac{1}{2}}=0.40$; $b'=c'=0$; $a=1.08$)	NONPOLAR N STATE, POLAR Z STATE ($b=c=0$; $a=0.90$; $b'=c'=a'/2^{\frac{1}{2}}$; $a'=0.68$)	N AND Z STATES BOTH POLAR ($b=c=a/2^{\frac{1}{2}}=0.40$; $b'=c'=a'/2^{\frac{1}{2}}$; $a'=0.68$)	
Q^2 (in $\text{\AA}^2$)	$0.087g^2$	0.033	0.078	0.063	0.057	0.001
f	$0.035g^2$	0.013	0.031	0.025	0.023	0.0004

* For the specific cases indicated the coefficients may be calculated from Eqs. (6) or (7).

† The observed f has been obtained from the absorption curves for acetone given by several authors (references 3-5, 30, 31) by using Eqs. (3) and (19) of reference 18. The value 0.0004 is an average for all these results. The correction used by Mulliken to take account of the effect of the solute (cf. reference 15, footnote 4, Table 6, p. 131) has not been employed because agreement between observed and calculated values appears to be better without the correction (cf. V. Henri and L. W. Pickett, J. Chem. Phys. 7, 439 (1939)). Such a correction would reduce the observed values of Q^2 and f from the values given above. The values for pure ketones other than acetone seem to be somewhat larger than for acetone (reference 3), the value of f for many pure ketones being about 0.0006. The results of some observers indicate that absorption in aldehydes may be somewhat weaker than in acetone (references 4, 5 and 32).

ing to the two terms in the linear combination for t_3 , with coefficients respectively those for s_C and z_C in t_3 .²² The Q integrals are expressed in angstrom units. All of the integrals are calculated for a C—O distance of 1.215 $\text{\AA}$, the distance observed in formaldehyde.²¹

Table II gives the values of Q^2 (in $\text{\AA}^2$) and of f , using Q^2 calculated from Eqs. (8) and (9). Several values, corresponding to different arbitrarily chosen degrees of polarity in the 1N and 1Z states, have been calculated from Eq. (9). The best "predicted" value of Q obtainable from Eq. (9) should lie within this range of values.

G. Conclusions

For most of the spectra considered by Mulliken the ratio of the calculated to the observed dipole strength for transitions analogous to the one considered here ranges between 1 and 5 for the AO and between 5 and 20 for the $LCAO MO$ approximation.^{9,10} The ratio of the dipole strength calculated here for the allowed transition to that observed for the longest wave-length absorption is from 35 to 75 by the AO approximation and at least 75 by the MO approximation (assuming $g=0.94$, the lowest possible value in the MO approximation). This, as was pointed out in Section II B, can be taken as satisfactory proof that the allowed transition does not correspond to the observed longest wave-length absorption in aldehydes and ketones. This absorption then most probably belongs to the type of forbidden transition proposed by Mulliken⁷ to explain the absorption in H_2CO ; i.e., a transition to the 1E state of (2). Further evidence corroborating this

conclusion will be advanced in the paper following.^{33a}

The assignment of the long wave-length absorption to this forbidden transition requires the allowed transition to the 1Z state to come at shorter wave-lengths, probably with an intensity near to that predicted from the calculated results given in Table II.

H. The intensity calculated using nonlocalized MO 's

The localized $LCAO MO$ wave functions used above are probably reasonably good $LCAO MO$ approximations. However, some tendency for the electrons to move throughout the molecule exists, and the intensity for the $^1N \rightarrow ^1Z$ transition for H_2CO will now be discussed using non-localized $LCAO MO$'s.

Electron configurations for H_2CO using non-localized MO 's have been given by Mulliken.⁷ These MO 's belong to three of the four species of the symmetry group $C_{2v}(a_1, b_2, \text{ and } b_1)$.³⁴ The MO 's belonging to species a_1 and b_2 will be denoted, respectively, by φ_i and ω_i . These non-localized MO 's may be written as follows:³⁵

Species a_1 : $\varphi_i = a_i\sigma + b_i s_C + c_i z_C + d_i z_O$,
 $i = 1, 2, 3 \text{ or } 4$

Species b_2 : $\omega_i = f_i\tau + h_i y_C + k_i y_O$, $i = 1, 2, \text{ or } 3$

Species b_1 : $x_C x_O = m x_C + n x_O$; $x_C \bar{x}_O = m' x_C - n' x_O$.

^{33a} H. L. McMurtry, J. Chem. Phys. 9, 241 (1941).

³⁴ Cf. R. S. Mulliken, Phys. Rev. 43, 279 (1933).

³⁵ Here σ and τ are combinations of the two hydrogen $1s$ AO 's, s_1 and s_2 , belonging, respectively, to representations a_1 and b_2 , and are defined as follows:

$$\sigma = (s_1 + s_2)/(2 + 2S)^{\frac{1}{2}}; \quad \tau = (s_1 - s_2)/(2 - 2S)^{\frac{1}{2}};$$

with

$$S = \int s_1 s_2 dv.$$

The b_1 MO 's here are identical with the localized x MO 's in (2).

In terms of these MO 's the electron configurations for the normal state and the excited states 1E and 1Z become:

$$\begin{array}{ll} ^1N \cdots (\varphi_1)^2 (\varphi_2)^2 (\omega_1)^2 (x_C x_O)^2 (\omega_2)^2, & ^1A_1 \\ ^3, ^1E \cdots \cdots \cdots (\omega_2) (x_C \bar{x}_O), & ^3, ^1A_2 \quad (10) \\ ^3, ^1Z \cdots \cdots \cdots (\omega_2) (\varphi_3), & ^3, ^1B_2. \end{array}$$

Q for the transition $N \rightarrow ^1Z$ now comes out as follows:

$$\begin{aligned} Q &= 2^{\frac{1}{2}} \int \omega_2 y \varphi_3 dv \\ &= 2^{\frac{1}{2}} [f_2(a_3 Q_{\tau\sigma} + b_3 Q_{\tau sC} + c_3 Q_{\tau zC} + d_3 Q_{\tau zO}) \\ &\quad + h_2(a_3 Q_{yC\sigma} + b_3 Q_{yCsC} + d_3 Q_{yCzO}) \\ &\quad + k_2(a_3 Q_{yO\sigma} + b_3 Q_{yOsC} + c_3 Q_{yOzC})]. \quad (11) \end{aligned}$$

Here any symbol such as Q_{ab} represents an integral of the form

$$\int a y b dv. \text{ Thus } Q_{\tau zC} = \int \tau y z_C dv.$$

While the relative magnitudes of the integrals appearing in Eq. (11) may be estimated, only rough values of their coefficients may be obtained. Examination shows that Q , according to Eq. (11), is greatly influenced by the signs and magnitudes of b_3 and c_3 . There is so much uncertainty in determining the signs and the relative magnitudes of these quantities that Eq. (11) cannot be used, at present, to evaluate Q even qualitatively.^{35a}

For any molecule other than formaldehyde, semilocalized MO 's, analogous to the nonlocalized MO 's of formaldehyde, may be constructed to describe the wave functions of the carbonyl group and its two attached atoms. The expression for the Q of the $^1N \rightarrow ^1Z$ transition then involves the AO 's of the atoms attached to the $C=O$ and therefore depends somewhat on the nature of the attached atoms.^{35a} The absorption intensity for this transition may be expected to change somewhat between molecules where the attached atoms differ markedly.

^{35a} In this laboratory Professor Mulliken and Dr. C. A. Rieke have made some calculations on the hyperconjugation energies in aldehydes and ketones. Their preliminary calculations yield the values 0.27, 0.06, and -0.96, respectively, for f_2 , h_2 and k_2 . (Coefficients analogous to these for acetone are, respectively, 0.30, 0.14, and -0.94.) Accordingly, the terms in which f_2 appears may be appreciable and the transition may not be very completely localized in the $C=O$ group.

I. The intensity of the forbidden transition

In aldehydes the intensity contributed to the "forbidden" transition because of the departures of the carbonyl wave functions from C_{2v} symmetry (see I. Introduction) might be expected to cause this transition to be stronger than in ketones where these departures are smaller. However, just the opposite appears to be the case experimentally, the longest wave-length

$C=O$ absorption apparently being stronger in ketones than in aldehydes³⁶ (cf. Table II, note).

A reasonable explanation is that the forbidden transition, which probably always obtains the major part of its intensity from electronic-vibrational perturbations, must be stronger in ketones than in aldehydes. A likely reason for such a difference is discussed in Section IV A.

IV. SPECTRA OF ALDEHYDES AND KETONES AT SHORTER WAVE-LENGTHS

A. Absorption between $\lambda 1900$ and $\lambda 1750$

The absorptions following next after the long wave-length regions in ketones,^{31, 37-39} acetaldehyde,³⁹ and formaldehyde,⁴⁰ come near $\lambda 1900$, $\lambda 1800$ and $\lambda 1750$, respectively. The existence of the region at $\lambda 1900$ in all of the ketones for which studies have been made shows that, in all likelihood, this transition is also characteristic of the carbonyl group. Apparently there is a shift toward shorter wave-lengths in aldehydes, where hydrogen atoms are substituted for alkyl groups. However, investigations on a larger number of aldehydes would be desirable to establish this with certainty.

In acetone the measured value of Q^2 for the $\lambda 1900$ absorption⁴¹ is about $0.032A^2$, in good

³⁶ A marked reduction in intensity is also observed for the longest wave-length absorption on going from diacetyl ($CH_3COCOCH_3$) to glyoxal ($HCOCOH$). (See references 4 and 30 for abs. curves of these molecules in hexane solution.)

³⁷ A. B. F. Duncan, J. Chem. Phys. **8**, 444 (1940), absorption of ketones in the Schumann region. (See also A. Duncan, J. Chem. Phys. **3**, 131 (1935) and A. Duncan, V. Ells and W. Noyes, J. Am. Chem. Soc. **58**, 1454 (1936).)

³⁸ W. A. Noyes, Jr., A. B. F. Duncan and Winston Manning, J. Chem. Phys. **2**, 717 (1934).

³⁹ G. Scheibe, F. Povenz and C. F. Linström, Zeits. f. physik. Chemie **B20**, 283 (1933).

⁴⁰ W. C. Price, J. Chem. Phys. **3**, 256 (1935).

⁴¹ Estimated by applying Eqs. (3) and (19) of reference 18 to the results of Ley and Arends (reference 31).

agreement with what might be predicted from the calculated values for the allowed transition from the carbonyl group (cf. Table II). This fact encourages the idea that the $\lambda 1900$ absorption may be identified with this allowed transition.

Forbidden transitions gain their intensities by perturbations from nearby allowed transitions, the effect being greater the less the difference in frequency between the two transitions.⁸ The suggestion that the $\lambda 1800$ and $\lambda 1900$ regions correspond, respectively, to the *allowed* transitions in aldehydes and ketones is strengthened by the fact that this transition can provide the perturbations causing the *forbidden* transition to appear at longer wave-lengths.⁷ Any reduction in the long wave intensity of aldehydes as compared to ketones can be explained if the adjacent strong regions are farther removed from the long wave-length absorption in aldehydes than in ketones. This appears to be true at least for acetaldehyde and formaldehyde.

Another possibility for explaining the $\lambda 1900$ region in ketones might be an $N \rightarrow V$ transition analogous to that producing the strong longest wave-length absorption in ethylene.^{14, 15, 42} This, however, can be excluded because a much higher intensity than that observed in ketones at $\lambda 1900$ is predicted for it.⁴³ Furthermore, estimates of the energies of the MO 's between which this transition takes place indicate that the absorption most probably comes at shorter wave-lengths than $\lambda 1800$.⁴⁴

⁴² Cf. reference 16(a), p. 373.

⁴³ The intensity for this transition, calculated by the writer in a manner similar to that used for the $N \rightarrow V$ of ethylene,¹⁴ predicts values of Q^2 equal to $0.033A^2$ and $0.8A^2$, according to the AO and $LCAO$ MO approximations, respectively. Empirically,¹⁴ the actual intensity is expected to be about midway between these values and should, in this case, be far larger than the Q^2 observed for the acetone absorption at $\lambda 1900$.

⁴⁴ The $N \rightarrow V$ transition would involve excitation of an electron from the $x_{C\bar{x}O}$ MO to the $x_{C\bar{x}O}$ MO . The energies of these MO 's have been calculated by the writer using methods similar to those which have been employed for ethylene (E. Hückel, *Zeits. f. Elektrochemie* **43**, 752 (1937)) but which have been designed to take account of the polarity of the carbonyl group. A comparison of the expressions for these energies for ethylene and the carbonyl group indicates that the two MO 's should be more widely separated in the latter case. The results are only qualitative, however, and no quantitative estimates of the separation of the $N \rightarrow V$ absorptions of the two groups could be made. The $N \rightarrow V$ absorption for ethylene comes near $\lambda 1800$.

Finally, a Rydberg transition might, perhaps, explain these bands. In H_2CO , however, the $\lambda 1750$ absorption does not seem to belong to any Rydberg series.⁴⁰ Duncan³⁷ finds that the band at $51,171\text{ cm}^{-1}$ in acetone can be included in a Rydberg series, but only if anomalous intensity changes among the bands in the series are overlooked.

To sum up, it may be said that these bands near $\lambda 1800$, represent a transition taking place mainly in the $C=O$ group. The absorption most probably comes from the allowed transition discussed above, although a Rydberg transition may contribute part or even all of the intensity.

B. Further absorption regions in ketones

Duncan³⁷ has photographed the spectra of several ketones in the ultraviolet and Schumann regions and finds that down to $\lambda 1500$ there is a close resemblance for the positions of the absorption regions in all of the molecules investigated. Following the $\lambda 1900$ region discussed above, there is a weaker region near $\lambda 1650$ and then a strong region near $\lambda 1550$ or $\lambda 1500$.

The $N \rightarrow V$ transition of the $C=O$ group can possibly explain the strong absorption near $\lambda 1500$ or $\lambda 1550$. It appears quite certain that this transition cannot lie at longer wave-lengths than these because no absorption of sufficient strength for such a transition is known. The $N \rightarrow V$ absorption may, however, lie at still shorter wave-lengths than $\lambda 1500$.⁴⁴

Further information concerning the intensities and positions of the carbonyl absorptions coming at shorter wave-lengths than $\lambda 1900$ would help in establishing the nature of the transitions giving the absorptions. This information is particularly lacking for aldehydes where results are available only for formaldehyde and, to a limited extent, for acetaldehyde.

V. SPECTRA OF THIO COMPOUNDS

Electronically the sulfur and oxygen atoms are very similar. In forming chemical bonds the $3p$ electrons of sulfur play the same role as the $2p$ electrons of oxygen.⁷ For this reason the absorptions from the $C=S$ group must be similar to those from the $C=O$ group. The lower ionization

TABLE III. Absorption regions from C=O and C=S groups.

MOLECULE	STRUCTURAL FORMULA*	REPORTED ABS. REGION (IN CM ⁻¹)	COLOR (PRODUCED BY LONGEST λ ABS.)	REF.†
Diethyl carbonate	$\begin{array}{c} \text{O} \\ \\ \text{Et}-\text{O}-\text{C}-\text{O}-\text{Et} \end{array}$	—	colorless	P.J.T.
Diethylthion-carbonate	$\begin{array}{c} \text{S} \\ \\ \text{Et}-\text{O}-\text{C}-\text{O}-\text{Et} \end{array}$	32,800	yellow	P.J.T.
Diethyl dithio carbonate	$\begin{array}{c} \text{O} \\ \\ \text{Et}-\text{S}-\text{C}-\text{S}-\text{Et} \end{array}$	40,580	colorless	P.J.T.
Diethyl trithio carbonate	$\begin{array}{c} \text{S} \\ \\ \text{Et}-\text{S}-\text{C}-\text{S}-\text{Et} \end{array}$	36,200	deep reddish orange	P.J.T.
Phosgene	$\begin{array}{c} \text{O} \\ \\ \text{Cl}-\text{C}-\text{Cl} \end{array}$	—	colorless (36,000)	H.
Thiophosgene	$\begin{array}{c} \text{S} \\ \\ \text{Cl}-\text{C}-\text{Cl} \end{array}$	32,000	orange-red** (23,000)	H.

* Et signifies the ethyl radical (C₂H₅).

† P.J.T.—J. E. Purvis, H. Jones, and H. S. Tasker, J. Chem. Soc. 97, 2287 (1910).

H.—V. Henri, *Structures des Molecules* (Paris, 1925). See pp. 88-92, and plates in back.

** Purvis, Jones and Tasker report only the color. The weak absorption in the two regions next following have been described by Henri.

potential of the 3p sulfur electrons should cause any long wave-length C=S absorption to lie at longer wave-lengths than the corresponding C=O absorption.

In a separate paper^{33a} it will be shown that the experimental results for molecules in which the C=S groups are conjugated to C=C groups bear out the above conclusions. The available data for molecules containing unconjugated C=S

groups are less extensive but appear always to be in harmony with what is expected. Table III lists the longest wave-length absorptions reported for several pairs of molecules which are identical except for the presence of a C=S group in one member of the pair where a C=O group occurs in the other. It seems evident, however, that the absorptions listed as "reported" in Table III are not the longest wave-length absorptions for the molecules given there. Thus, the absorptions (probably weak) which cause the color of the molecules containing the C=S group are not recorded.⁷ Similarly, it seems evident that the weak C=O absorption is not included. For this reason, the column describing the color of the respective molecules is included in Table III.

In molecules containing the C=O group, the absorption region following next after the weak longest wave-length region appears to be characteristic of this group (cf. Section IV A). It is, therefore, reasonable to suppose that the regions reported in Table III for the stronger C=S absorptions come from a transition characteristic of this group and analogous to that producing the λ 1900 region in ketones. The shift toward longer wave-lengths can be explained by the low ionization potential of the 3p sulfur electrons.

The author is indebted to Professor R. S. Mulliken for suggesting this work and for giving continued assistance and encouragement during its progress. He wishes also to express appreciation to his father without whose help and encouragement his graduate studies might not have been possible. Thanks are due to his wife for aiding in the preparation of the manuscript and for lending assistance in many other ways.

The Long Wave-Length Spectra of Aldehydes and Ketones

Part II. Conjugated Aldehydes and Ketones

HENRY L. MCMURRY

Ryerson Physical Laboratory, University of Chicago, Chicago, Illinois

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An interpretation of the long wave-length absorption regions of conjugated aldehydes and ketones is given. The strong regions can be assigned to transitions of the $N \rightarrow V_1$ type known to produce the intense long wave-length absorption in polyenes. The weak absorption regions, which are characteristic of the carbonyl group, can be explained as arising from the type of transition previously proposed to explain the weak carbonyl absorption in saturated aldehydes and ketones. This transition involves the excitation of a loosely bound electron occupying a nonbonding orbital lying in the molecular plane and across the C=O direction, to an excited molecular orbital with a node in this plane. In conjugated molecules several of these excited MO 's exist and transitions to them all are predicted. The longest wave-length carbonyl absorption represents a transition to the

lowest of these MO 's and the observed shift of this absorption toward longer wave-lengths with each addition to the number of conjugated bonds in the chain can be explained by the fact that this lowest excited MO is reduced in energy as the length of the chain increases. The longest wave-length absorption for quinones and for aromatic aldehydes and ketones can be explained by the same process as that producing this absorption in chain molecules. The long wave-length spectra of molecules containing conjugated C=S groups are shown to be similar to those for the analogous molecules containing C=O groups. The absorption from the C=S group is observed at longer wave-lengths because the orbital from which excitation comes is less firmly bound than in C=O.

I. INTRODUCTION

THE long wave-length absorption of a conjugated aldehyde or ketone [a molecule with a skeleton consisting of a conjugated chain of the form $(C=C)_n - C=O$ or $O=C - (C=C)_n - C=O$] is characterized by a strong absorption region which is apparently always followed at still longer wave-lengths by a much weaker absorption.¹⁻³

The strong absorption is, without doubt, produced by the same $N \rightarrow V_1$ type of transition which causes the appearance of the intense long wave-length absorption found in the spectra of polyene molecules.⁴ As is the case for polyenes, this strong absorption in conjugated aldehydes and ketones shifts toward longer wave-lengths as the number of conjugated groups increases.

The weak absorption region has no analog in the spectra of polyenes and is definitely to be associated with the presence of the C=O group. In all likelihood the mechanism of the transition

is similar to that producing the weak absorption near $\lambda 2900$ in saturated aldehydes and ketones.⁵ The nature of this transition in the unconjugated C=O group has been discussed in a previous article⁶ (hereafter referred to as I). The present discussion shows that essentially the same mechanism will explain the observed absorption in the conjugated aldehydes and ketones.

For future reference the positions and approximate intensities (in terms of f values⁷) for the strong and weak absorptions of several conjugated aldehydes and ketones are listed in Table I. Also included for comparison are the strong regions in several polyenes.

II. MECHANISMS FOR THE LONG WAVE-LENGTH ABSORPTIONS IN CONJUGATED ALDEHYDES AND KETONES

A. The strong absorption

The strong absorption region in any conjugated aldehyde or ketone is so similar in position

¹ A. Smakula, *Angew. Chemie* **47**, 657 (1934), strong absorption bands of conjugated aldehydes and ketones.

² K. W. Hausser, R. Kuhn, A. Smakula, and M. Hoffer, *Zeits. f. physik. Chemie* **B29**, 371 (1935), strong absorption regions in conjugated aldehydes and ketones.

³ *Int. Crit. Tab.*, Vol. V (also see Table I for further references).

⁴ R. S. Mulliken, *J. Chem. Phys.* **7**, 364 (1939).

⁵ Ref. 3, and the following: E. Eastwood and C. P. Snow, *Proc. Roy. Soc.* **149A**, 434 (1935); F. O. Rice, *Proc. Roy. Soc.* **91A**, 76 (1914-1915); J. Bielecki and V. Henri, *Ber. d. D. Chem. Ges.* **46**, 3627 (1913).

⁶ H. L. McMurry, *J. Chem. Phys.* **9**, 231 (1941) (hereafter referred to as I). See also H. L. McMurry and R. S. Mulliken, *Proc. Nat. Acad. Sci.* **26**, 312 (1940).

⁷ Cf. R. S. Mulliken, *J. Chem. Phys.* **7**, 14 (1939), also I.

TABLE I. Absorption regions in aldehydes and ketones.

NUMBER OF CONJUGATED BONDS	MOLECULE	STRONG ABSORPTION				WEAK ABSORPTION		
		STRUCTURAL FORMULA	POSITION (IN CM ⁻¹) ²	f ³	REF. ¹	POSITION (IN CM ⁻¹) ²	f ³	REF. ¹
0	Ethylene	CH ₂ :CH ₂	58000 (vap.)	st.	R.M.	—	—	—
	Acetone	CH ₃ COCH ₃	65000 ⁶ (vap.)	st. ⁵	I	36500 (hex.)	0.0004	I
2	Butadiene	CH ₂ :CHCH:CH ₂	46000 (hex.)	0.53	Sm.	—	—	—
			46000 (vap.)	—	P.W.			
	Acrolein	CH ₂ :CHCHO	50700 (hex.)	.69	I.C.T. Fig. 73	30000 (vap.)	0.0004	B.Y.R.
						30000 (hex.)	.0003	Lüthy
	Crotonaldehyde	CH ₃ CH:CHCHO	47200 (hex.)	.40	H.K.S.H. Sm.	30500 (vap.)	.0004	B.Y.R.
			48000 (hex.)	.80 ⁹	I.C.T. Fig. 73	30000 (hex.)	.0005	I.C.T. Fig. 73
	Ethylidenacetone	CH ₃ CH:CHCOCH ₃	46500 (hex.)	.22	Sm.	colorless	—	—
	Mesityloxiide	(CH ₃) ₂ C:CHCOCH ₃	43000 (hex.)	.23	I.C.T. Fig. 74	31000 (hex.)	.001	I.C.T. Fig. 74
			42600					
	Citral	(CH ₃) ₂ C:CHCH ₂ CH ₂	43200 (hex.)	.28	Sm.	31000 (hex.)	.0016	I.C.T. Fig. 74
		C(CH ₃):CHCHO	42800 (hex.)	1.03 ⁹	I.C.T. Fig. 74			
			54000 (hex.)	—	Sm.			
	Glyoxal	CHOCHO	—	—	—	22000 (hex.)	(.00004)	I.C.T. Fig. 85
						36000	(.00005)	I.C.T. Fig. 85
	Diacetyl	CH ₃ COCOCH ₃	57000 ⁷ (vap.)	st. ⁵	E.	24000 (hex.)	(.0003)	I.C.T. Fig. 85
							.0002	A.A. ⁴
						35500 (hex.)	(.0003)	I.C.T. Fig. 85

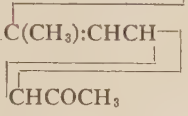
and intensity to that for the polyene molecule having the same number of conjugated bonds⁸ that the transition process must be the same in each case.

⁸ See K. Hausser, Zeits. f. tech. Physik 15, 10 (1934). Fig. 4 plots the absorption positions against the number of conjugated C=C bonds. In the present article the C=O groups are included in counting the number of conjugated bonds.

The nature of the energy levels involved in this transition in polyenes has been discussed by Hückel,⁹ Mulliken⁴ and others. It is believed that the carbon atoms which are members of a conjugated chain lie in one plane. The bonds between adjacent carbon atoms are produced by

⁹ E. Hückel, Zeits. f. Electrochemie 43, 752, 827 (1937), a general review discussing the electronic structures of unsaturated hydrocarbons.

TABLE I.—Continued.

NUMBER OF CONJUGATED BONDS	MOLECULE	STRONG ABSORPTION				WEAK ABSORPTION		
		STRUCTURAL FORMULA	POSITION (IN CM ⁻¹) ²	<i>f</i> ³	REF. ¹	POSITION (IN CM ⁻¹) ²	<i>f</i> ³	REF. ¹
3	Hexatriene	CH ₂ :CHCH:CHCH:CH ₂	40000 ⁸	—	M.S.	—	—	—
	Hexadienal	CH ₃ CH:CHCH:CHCHO	39100 (hex.)	0.61	H.K.S.H.	nearly colorless	—	K.H.
	Crotyliden-acetone	CH ₃ CH:CHCH:CHCOCH ₃	37900 (hex.)	.34	Sm.	yellowish	—	M.
	Pseudoionone	(CH ₃) ₂ C:CHCH ₂ CH ₂	35400 (hex.)	.34	Sm.	yellow	—	T.
			54000	—	Sm.			
	Butenedial	CHOCH:CHCHO	—	—	—	yellow	—	W.M.
4	Octatrienal	CH ₃ CH:CHCH:CH 	32700 (hex.)	.75	H.K.S.H.	weak yellow	—	K.H.
		CH:CHCHO						
5	Decatetraenal	CH ₃ CH:CHCH:CH 	30000 (hex.)	—	H.	—	—	—
		CH:CHCH:CHCHO						

¹ A.A. G. Almy and S. Anderson, J. Chem. Phys. **8**, 805 (1940).B.Y.R. J. C. Blacet, W. G. Young and J. G. Roof, J. Am. Chem. Soc. **59**, 608 (1937).

E. V. R. Ells, reference 16.

H. K. W. Hauser, reference 8.

H.K.S.H. K. Hauser, R. Kuhn, A. Smakula and M. Hoffer (reference 2).

I.C.T. International Critical Tables, Vol. V.

K.H. R. Kuhn and K. Hauser, Ber. d. D. Chem. Ges. **64**, 1977 (1931).Lüthy A. Lüthy, Zeits. f. physik. Chemie **A107**, 285 (1923).

M.S.

M.

P.W.

R.M.

T.

Sm.

W.M.

I

st.

A. K. Macbeth and A. W. Stewart, J. Chem. Soc. **111**, 829 (1917).H. Meerwein, Liebigs Annalen, **A358**, 86 (1908)

W. C. Price and A. D. Walsh, reference 20.

R. S. Mulliken, J. Chem. Phys. **7**, 20 (1939).F. Tiemann, Ber. d. D. Chem. Ges. **31**, 842 (1898).

A. Smakula, reference 1.

A. Wohl and B. Mylo, Ber. d. D. Chem. Ges. **45**, 1748 (1912).

See I (reference 6).

Strong absorption.

² The terms (hex.) and (vap.) refer, respectively, to absorption curves for molecules in hexane solution or in the vapor phase.

³ These *f* values have been obtained by applying Eqs. (3) and (19) of reference 7 to the absorption curves given in the references. No correction has been made for the effect of the solvent (see note for Table II of I). In many cases the nature of the absorption curves makes accurate estimation of *f* difficult. The cases for which this is particularly true have been placed in parentheses. In these cases the error in *f* may be as large as 50 percent or more. In the present work the order of magnitude is most important and such deviations do not affect the conclusions at all.

⁴ This *f* value has been calculated from the lifetime in the excited state (of the order of 10⁻⁹ sec.). (Cf. e.g. reference 7, Eq. (12)).

⁵ No estimate of the *f* value is possible but the absorption is very intense.

⁶ The absorption in acetone corresponding to that in the conjugated ketones may lie at higher frequencies than 65,000 cm⁻¹. This frequency appears to be a lower limit for this transition (see I).

⁷ It is not certain that this region corresponds to the strong transition in the other conjugated aldehydes and ketones. However, the evidence strongly suggests that this is the case (see text).

⁸ This value is only approximate.

⁹ The half-widths of the absorption regions are nearly the same for both authors. The maximum value of the absorption coefficient is much higher for the I. C. T. curve.

electrons in two types of molecular orbitals (*MO*'s). One of these (the σ type) is concentrated along the C—C direction and may be taken as localized between just two carbon atoms. The second (called the π or α type) possesses a node in the molecular plane and is best taken as nonlocalized, i.e., extending along the entire system of conjugated bonds. The α type electrons exert bonding or antibonding effects across both the "single" and "double" bonds in the chain.¹⁰

This influence prevents rotations around the C—C axes and thus enforces the plane structure for the molecule.

The symmetry of the α *MO*'s is such that they do not mix with other types of *MO*'s. The forms and energies of the α *MO*'s may be obtained by assuming that the electrons in all the other *MO*'s act only as screening electrons.^{9,10} In the normal state of any polyene chain molecule the

The "double" bond in a conjugated chain is less strong than in ethylene (C₂H₄) while the "single" bond becomes stronger than in ethane (C₂H₆).

¹⁰ Cf. J. E. Lennard Jones, Proc. Roy. Soc. **158A**, 280 (1937); W. G. Penney, Proc. Roy. Soc. **158A**, 306 (1937).

half of the π MO 's of lowest energy are populated with two electrons each. Hückel's treatment shows that as the number of conjugated bonds increases the energy of the highest π MO occupied in the normal state rises while that of the lowest excited MO falls. This means that the absorption produced by excitation from the former of these MO 's to the latter is shifted toward longer wave-lengths as the number of conjugated bonds increases. This shift of the absorption position with increasing conjugation is observed to be one of the striking characteristics of the long wave-length absorption in polyenes and is definite proof that the transitions are of the type just described.¹¹ These transitions are known as $N \rightarrow V_1$ transitions and reasons for their strong intensity have been given by Mulliken.⁴

The bonds between the carbon and oxygen atoms in the $C=O$ group are formed in essentially the same way as those in the $C=C$ group. Therefore, the nonlocalized π MO 's of a conjugated chain which includes a $C=O$ group necessarily involve the π electrons of this group and are similar in form to those for the polyene chain containing an equal number of double bonded groups. A $C=O$ group is, therefore, expected to produce an effect similar to that for a $C=C$ group on the position of an $N \rightarrow V_1$ absorption. The strong absorptions in crotonaldehyde and hexadienal are, respectively, near those for butadiene and hexatriene (cf. Table I). This is satisfactory proof that they correspond to $N \rightarrow V_1$ transitions between π MO 's which cover the entire chain inclusive of the $C=O$ group. The existence of a *second* strong region in citral and pseudoionone may be due to the unconjugated $C=C$ (see reference 28).

B. The weak absorption

The weak absorption region characteristic of the $C=O$ group is apparently always found on the long wave-length side of the $N \rightarrow V_1$ absorp-

tion.³ In the singly conjugated molecules like acrolein, this absorption is observed to be shifted toward the visible from the weak region near $\lambda 2900$ which is characteristic of the unconjugated $C=O$ group. The color of the higher conjugated aldehydes and ketones is good evidence that this absorption is shifted toward still longer wave-lengths as the number of conjugated double bonds increases beyond two.

The transition proposed to explain this absorption by unconjugated $C=O$ groups involves excitation of an essentially nonbonding electron localized largely on the oxygen atom to the excited π MO of the $C=O$ group.⁶ The MO (called y_0 in I) from which excitation comes lies in the molecular plane and has a node on the $C-O$ axis.

In conjugated molecules transitions from a similar nonbonding MO to each of the several excited π MO 's are expected. The longest wave-length of these absorptions should shift toward increasing wave-lengths as the number of conjugated groups increases and brings the energy of the lowest excited π MO down. This behavior is observed in all the cases for which the weak $C=O$ absorption has been reported (cf. Table I) and may be taken as very good proof that this absorption is due to the type of transition described.

In molecules where the $C=O$ group is not conjugated the low intensity of the absorption is explained by the fact that the transition is essentially forbidden.⁶ When, however, one (or two) $C=O$ groups are at the end (or ends) of a conjugated chain the transition is no longer forbidden by the electronic selection rules, since the symmetry of the skeleton is, in general, different from C_{2v} . However, the intensity gained in this way should be very slight—in fact, too slight to explain the observed absorption intensity for the long wave-length regions in these molecules.

This may be shown by calculating the theoretically expected intensity for the transition¹² and comparing with the observed intensity for the longest wave-length absorption (cf. I). The

¹¹ Absorption transitions between MO 's of the σ type do not show this behavior. Thus the spectra of long unconjugated chains where the carbon atoms are held together by single (σ) bonds show very little tendency to shift toward the visible. [Cf. R. S. Mulliken, J. Chem. Phys. 7, 128 (1939). The fact that these molecules show no absorptions above $\lambda 2000$ is good evidence that σ MO 's do not behave like those of the π type.] Essentially the σ MO 's may be thought of as being localized between only two carbon atoms.

¹² Note that the calculation reported here is for transitions analogous to the "forbidden" transition (${}^1N \rightarrow {}^1E$ in I) and does not correspond to the calculation of the ${}^1N \rightarrow {}^1Z$ intensity reported in I.

expression for the dipole moment Q (cf. reference 7, Eq. (4)) is found to involve, among others, electric moment integrals between the non-bonding $2p_y$ oxygen AO 's and the $2p_x$ AO 's appearing in the $LCAO$ expression for the lowest excited π MO . The integrals of this type involving the $2p_x$ AO 's of the oxygen atom and its adjacent carbon atom are zero by symmetry. The remaining integrals are small and tend to cancel. For diacetyl the predicted intensity, estimated according to the criteria of I, is less than one-fifth of that observed for the weak absorption near $\lambda 4000$. This means that the transitions producing the weak long wave-length absorptions in conjugated aldehydes or ketones, although not, strictly speaking, electronically forbidden, must obtain most of their observed intensities after the manner of forbidden transitions, that is, by electronic-vibrational interaction.¹³

III. LOW ELECTRONIC STATES OF CONJUGATED ALDEHYDES AND KETONES

A. Electron configurations

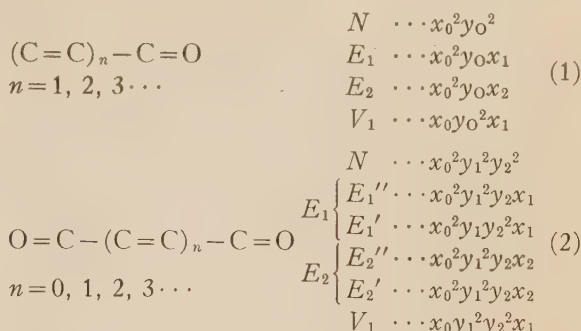
The MO electron configurations for the normal and low excited states of conjugated aldehydes and ketones will here be expressed with the omission of all MO 's except those from and to which excitation takes place. In the following, x_0 and x_{-1} refer, respectively, to the highest and next highest energy π MO 's which are occupied in the normal state. The lowest excited π MO will be written as x_1 , while higher excited π MO 's, if needed, will be denoted by x_2, x_3 , etc. in the order of their energy. For molecules containing only one $C=O$ group the nonbonding MO which is largely localized on the oxygen atom is written simply as y_0 , in conformity with the notation used in (I) for the analogous MO of the unconjugated $C=O$ group. In molecules, like diacetyl, where $C=O$ groups are at the ends of a conjugated chain, the $2(p_y)_O$ AO 's of the end atoms interact slightly producing two MO 's. These can be described by taking positive and negative linear combinations of two y_0 AO 's of the end atoms and will be written y_1 and y_2 .¹⁴

¹³ G. Herzberg and E. Teller, *Zeits. f. physik. Chemie* **B21**, 410 (1933).

¹⁴ These MO 's have the following forms:

$$\begin{aligned} y_1 &= (y_{Oa} - y_{Ob})2^{-\frac{1}{2}} \\ y_2 &= (y_{Oa} + y_{Ob})2^{-\frac{1}{2}} \end{aligned}$$

The electron configurations for the normal and low excited states may be written as follows:



In molecules containing two $C=O$ groups the E states come in pairs (E' and E'' states) which are nearly degenerate. The transition to only one of these states is allowed by the electronic selection rules.¹⁵ However, these transitions can be best explained as obtaining most of their intensities from perturbations due to electronic-vibrational coupling¹³ and, under these circumstances, transitions to all of the E states will appear. Therefore, it is not possible, at present, to distinguish experimentally between transitions to either of the states in a degenerate pair. Hence, each such pair will be designated by a single symbol which is the same as that used to denote the corresponding state in the molecule containing the same number of conjugated bonds but possessing only one $C=O$ group (cf. (2) above).

Figure 1 shows the energy levels corresponding to the states given in (1) and (2). These energy levels have been obtained from the spectrum by ascribing the absorption regions listed in Table I to transitions between the normal and excited states of (1) or (2). Also included are the V_1 states for several polyenes.

where y_{Oa} and y_{Ob} refer to the $2(p_y)_O$ AO 's of the oxygen atoms at the ends of the chain.

The interactions between these MO 's depend on the separation of the two end atoms and are probably very small for atoms as far apart as those in diacetyl and glyoxal.

¹⁵ In a molecule like diacetyl where the $O=C-C=O$ skeleton possesses the symmetry C_{2h} the lowest excited MO (x_1) belongs to the a_u representation of this point group and is analogous to that for butadiene (cf. R. S. Mulliken, *J. Chem. Phys.* **7**, 121 (1939), Tables I and II). The MO 's y_1 and y_2 belong, respectively, to the representations a_g and b_u of C_{2h} . Transitions between y_1 and x_1 are allowed with an $\pi(a_u)$ electric moment. The transition from y_2 to x_1 is forbidden since there is no component of the electric moment belonging to the b_2 representation of C_{2h} .

B. Discussion

The assignments for the $N \rightarrow V_1$ transitions of all of the molecules, except perhaps diacetyl, seem to be quite definite. Diacetyl is the only molecule containing two conjugated C=O groups which has been studied at wave-lengths below 2000Å. The intense absorption found at $\lambda 1750$ in this molecule¹⁶ occurs well above the first very strong ketone region at $\lambda 1550$. The $\lambda 1550$ region is the longest wave-length absorption capable of being identified as the $N \rightarrow V$ transition of the unconjugated C=O group.⁶ Therefore, the $\lambda 1750$ region of diacetyl agrees in position and intensity with what is expected for the $N \rightarrow V_1$ transition of two conjugated C=O groups.

There is also a region at $\lambda 1970$ in diacetyl but its intensity is too low, and its separation from the $\lambda 1550$ region in ketones is too large, to permit its being identified as the $N \rightarrow V_1$ transition. However, it does correspond well in intensity to the $\lambda 1900$ region of the saturated ketones and very probably arises from the same type of transition. The fact that this diacetyl absorption is not shifted greatly from that in ketones is in harmony with the behavior expected for a transition of the $N \rightarrow {}^1Z$ type described in I. This transition involves the y MO's and excited MO's of the σ type which are not expected to be changed greatly in energy when the C=O groups are conjugated (see reference 11).

The $N \rightarrow E_1$ absorptions for most aldehydes and ketones are known either from direct observation or, indirectly, because of the color they produce. The $N \rightarrow E_2$ regions, however, have been found only in diacetyl and glyoxal. Apparently in other molecules the $N \rightarrow E_2$ regions are covered by the $N \rightarrow V_1$ absorptions, or possibly they fall at shorter wave-lengths than those for which observations have been made.

C. Energies of the x and y_0 MO's

It is possible, using the available spectroscopic data, to make suggestions concerning the relative energies of the x and y_0 MO's in some of these molecules.

The lowest I.P. (ionization potential) of any molecule gives the term value of its most loosely bound electron. Mulliken¹⁷ has shown that in ketones and aldehydes this I.P. almost surely corresponds to removal of a y_0 electron—a



FIG. 1. Energy levels for conjugated aldehydes and ketones. Here X and Y stand for C=O and C=C groups, respectively. From right to left the energy levels shown are for ethylene, butadiene, crotonaldehyde, hexatriene, hexadienal, octatetraene, octatrienal, decatetraenal, butenedial, diacetyl and acetone. The dotted lines indicate predicted states which have not been observed. Their positions are probably not accurate (transitions to the predicted E_1 states of butenedial, octatrienal, and pseudoionone, must be responsible for their weak yellow colors).

conclusion which the present work corroborates. The theoretical interpretation of the longest wave-length absorption in ethylene and in polyenes shows that the lowest I.P.'s of these molecules must correspond to removal of an x_0 electron.

A knowledge of the x_0 term value and the position of the $N \rightarrow V_1$ absorption, or of the y_0 term value and the $N \rightarrow E_1$ absorption, allows an estimate to be made of the term values of the x_1 MO.¹⁸ In the aldehydes and ketones, where the x_0 I.P. is not known, it can be estimated from the position of the $N \rightarrow V_1$ transition, provided the term value of the x_1 MO can be found in the above manner.

¹⁸ This procedure involves the assumption that the MO's in any of these molecules have definite energies which are the same in all of the states considered here (N , E , and V states). Furthermore, the energy difference between the normal and excited states is assumed to give the difference in energy between the MO's from and to which excitation takes place. Strictly speaking, however, neither of these assumptions is true. Thus, the energy of any MO is determined by the charge distribution in the electronic state and, in excited states, this will vary with the MO from which excitation has taken place. Furthermore, the difference in energy between two states is not given simply by the difference in energy of the MO's involved in the transition, but is also determined by electronic interactions which depend on the form and symmetry of the wave functions for the states. These also change from one state to another. In the present qualitative discussion the above changes are neglected.

¹⁶ V. R. Ellis, J. Am. Chem. Soc. **60**, 1864 (1938).

¹⁷ R. S. Mulliken, J. Chem. Phys. **3**, 564 (1935).

Existing data can, in this way, be used to determine the approximate term values of the x MO 's in ethylene, butadiene and acetone. Thus the x_0 term values of ethylene¹⁹ and butadiene²⁰ are known from Rydberg series data to be 10.45 v and 9.02 v, respectively. Similar data give a term value of 10.2 v for the y_0 MO in acetone.²¹ The $N \rightarrow V$ and $N \rightarrow E$ transitions for these molecules can be found from Table I and Fig. 1. Price and Walsh²⁰ also report a region near $\lambda 1760$ in butadiene which they assign to the $N \rightarrow V_{2,3}$ transition. This assignment is in agreement, as far as the position of the absorption is concerned, with some suggestions of Mulliken.²² If correct, it serves to determine the term values of the x_2 and x_{-1} MO 's.²³

The term values of the x MO 's in crotonaldehyde and diacetyl, as well as some other conjugated aldehydes and ketones, could mostly be determined if the I.P.'s of the y_0 MO 's were known for these molecules. However, their spectra have not been investigated far enough into the vacuum region to supply the data needed and it is necessary to estimate values for these I.P.'s.

Price and his collaborators^{19,20} have shown that the substitution of alkyl groups for the hydrogen atoms in ethylene and butadiene raises the energies of their x MO 's. They attribute this to a transfer of charge from the alkyl groups toward the double bonded atoms. It seems probable that hyperconjugation between the methyl groups and these atoms may also play a part in altering the energies of the x MO 's.²⁴ Under any circumstances, the effects of the alkyl groups are very pronounced as can be seen from the fact that in tetramethyl ethylene, where four methyl groups are attached to a single C=C group, the energy of the x_1 MO is apparently higher than the energies of the x_2 MO 's in butadiene, isoprene, and β , γ dimethyl buta-

diene.²⁵ Simplified calculations,²⁶ which do not take account of differences in charge transfer, electronic interactions, and hyperconjugation effects between molecules, predict the energy of the x_1 MO of an unconjugated C=C group to be between the energies for the x_1 and x_2 MO 's of a conjugated diene.

When alkyl groups are attached to a C=O the energies of both the x and y_0 MO 's are expected to be altered. Here the effect due to charge transfer may be quite large because of the electronegativity of the oxygen atom. The effect of the alkyl groups on the I.P. of the y_0 MO can be seen by noting that the respective I.P.'s of acetone²¹ and formaldehyde²⁷ are 10.2 v and 10.9 v. In diacetyl, where there is only one methyl group per C=O, the charge transfer effect should be smaller and the y_0 MO energy should be between those for acetone and formaldehyde. In crotonaldehyde there is no methyl group attached to the C=O but the y_0 MO may still be raised in energy due to transfer of charge along the chain.

In Fig. 2 the relative energies of the x and y_0 MO 's, as determined from spectroscopic data, are shown for several of the molecules considered here. The MO 's in diacetyl and crotonaldehyde have been fixed by arbitrarily assuming the y_0 I.P. to be the same in each of these molecules and to have a value of 10.4 v. The x_1 MO of acetone is then found to be higher in energy than the two excited x MO 's in diacetyl. This behavior has already been noted between the x_1 MO of tetra methyl ethylene and the x_1 and x_2 MO 's of several conjugated dienes. In acetone and diacetyl this may be explained if the charge transfer and hyperconjugation effects are larger in acetone, where two methyl groups are attached to a single C=O, than in diacetyl where there is only one methyl group per C=O.

The energy of the x_0 MO of acetone is not known definitely but must be at least 65,000 cm^{-1} below the x_1 MO since the $N \rightarrow V$ absorption for this molecule apparently cannot lie at longer

¹⁹ W. C. Price and W. T. Tutte, Proc. Roy. Soc. A174, 207 (1940).

²⁰ W. C. Price and A. D. Walsh, Proc. Roy. Soc. A174, 220 (1940).

²¹ A. B. F. Duncan, J. Chem. Phys. 3, 131 (1935).

²² R. S. Mulliken, J. Chem. Phys. 7, 121 (1939).

²³ The simple theory (reference 22) shows that in butadiene the separation of the x_2 and x_1 MO 's is the same as that for the x_0 and x_{-1} MO 's. In the present case, an estimation of the former separation, together with the known term value of the x_0 MO , enables the x_{-1} term value to be found.

²⁴ R. S. Mulliken, J. Chem. Phys. 7, 339 (1939).

²⁵ This statement is based on estimates made using the I.P.'s and $N \rightarrow V$ absorption regions reported for these molecules by Price and his collaborators (references 19 and 20).

²⁶ These calculations are like those reported in I, reference 44.

²⁷ W. C. Price, J. Chem. Phys. 3, 256 (1935).

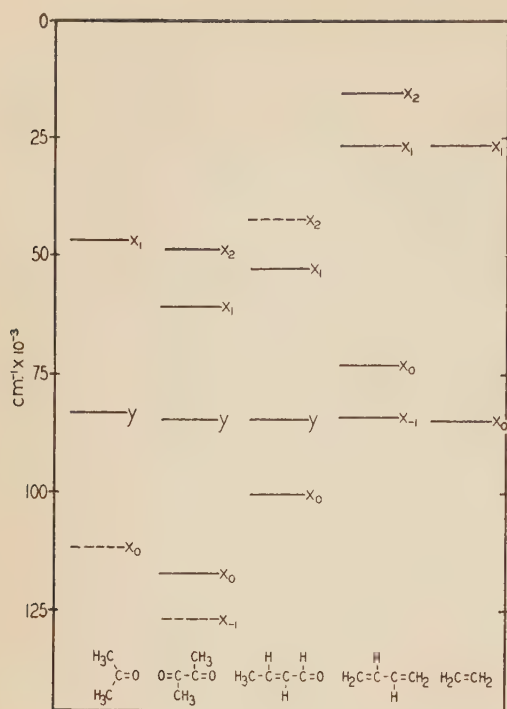


FIG. 2. Relative energies of x and y MO's. Note: The energies are for the x and y MO's described in Section III A. Here the symbol y is used to designate the y_0 , and the degenerate y_1 and y_2 , MO's of Eqs. (1) and (2) respectively. The dotted lines denote energy levels which can only be tentatively assigned due to lack of complete information. See text concerning location of MO's in diacetyl and crotonaldehyde.

wave-lengths than $\lambda 1500$.⁶ This places the x_0 MO of acetone somewhat above that of diacetyl—which is consistent with the expected influence of the alkyl groups in acetone. The x_{-1} MO of diacetyl has not been found. However, the simple theory²⁶ predicts that the separation of the x_0 and x_{-1} MO's in diacetyl is less than for the x_1 and x_2 MO's and this permits at least a rough assignment to be made for the position of the x_{-1} energy. Similarly, the x_0 and x_{-1} MO's in butadiene are predicted to be separated by the same amount as the x_1 and x_2 MO's. In this way the x_{-1} MO has been located for this molecule.

The x_1 and x_2 MO's of diacetyl are observed to be about $12,500\text{ cm}^{-1}$ apart. A similar separation can be expected for crotonaldehyde and if present would require the $N \rightarrow E_2$ absorption to appear somewhere around $40,000\text{ cm}^{-1}$. The absorption curves for crotonaldehyde³ show that the $N \rightarrow V_1$ absorption would cover any weak

region at $40,000\text{ cm}^{-1}$. In acrolein the $N \rightarrow V_1$ region appears at higher frequencies but there is still no evidence of the $N \rightarrow E_2$ region.

The available intensity data indicate that the $N \rightarrow V_1$ absorption in ketones and in citral may be less intense than in some of the corresponding aldehydes. In several cases the ratio of intensities for the two types of molecules is as much as two. Mulliken⁴ has shown that the intensities of the $N \rightarrow V$ transitions depend on the shape of the molecules, a *trans* arrangement of the two conjugated double bonds giving maximum $N \rightarrow V_1$ intensity and a *cis* arrangement a much lower intensity. He finds that any change tending to decrease the strength of the $N \rightarrow V_1$ absorption should increase the intensity for transitions to other V states.²⁸ This may mean that the conjugated aldehyde molecules have mostly a *trans* arrangement, the conjugated ketone molecules more nearly (or in a larger proportion of the molecules) a *cis* arrangement.

IV. QUINONES AND AROMATIC ALDEHYDES AND KETONES

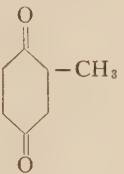
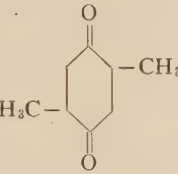
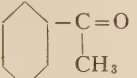
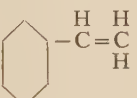
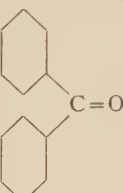
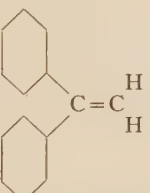
Many molecules contain C=O groups conjugated to the C=C groups in aromatic or quinoid rings. These compounds should show the weak absorption characteristic of the presence of the C=O group. As always, this is expected to be the longest wave-length absorption for the molecule concerned. Table II gives a few examples which show that this is the case. The absorptions of acetophenone and benzaldehyde may be compared directly with that of styrene which contains a C=C group in place of the C=O group present in the first two molecules. The molecules possessing the C=O group have absorption regions at $\lambda 3300$ (longest wave-length absorption) and $\lambda 2800$, while styrene has the $\lambda 2800$ region as its longest wave-length absorption. Similarly, the C=O group in benzophenone produces a weak longest wave-length absorption at $\lambda 3400$ which is completely lacking in 1,1 diphenylethylene. These molecules differ only

²⁸ In pseudoionone and citral, both of which have comparatively low $N \rightarrow V_1$ intensities, there is a region at $\lambda 1850$ which may conceivably be due to the $N \rightarrow V_2$ transition. However, this absorption can also be explained as the $N \rightarrow V$ transition of the unconjugated C=C group or as a possible Rydberg transition. Further studies on the spectrum at shorter wave-lengths would be necessary before any definite assignment could be made.

in that the former has a C=O group where the latter possesses a C=C group. Except for the appearance of the C=O absorption at $\lambda 3400$, the long wave-length spectra of the two molecules are very similar.

With this evidence as a basis, the longest wave-length absorptions of other molecules containing the C=O group, such as the quinones, may very probably be identified with transitions of the $N \rightarrow E_1$ type.

TABLE II. Absorption of quinones, phenones, and related compounds.

MOLECULE	STRUCTURAL FORMULA	LONGEST λ REGION ³ (POSITION IN CM ⁻¹)	f^2	NEXT ABS. REGION ³	f^2	REF. ¹
<i>p</i> -Benzoquinone		22400(hex.)	0.0003	36000(hex.)	(0.008)	L.
Toluquinone		22600(hex.)	.0003	32500(hex.)	(.007)	L.
<i>p</i> -Xyloquinone		23000(hex.)	.0003	33200(hex.)	(.005)	L.
Acetophenone		31200(alc.)	.0006	35900(alc.)	.014	B.H.
Benzaldehyde		30500(alc.)	(.0006)	35600(alc.)	.02	B.H.
Styrene		—	—	34300	—	Ley
Benzophenone		29500(hex.)	.002	39200(hex.)	(.4)	I.C.T. Fig. 88
1,1 Diphenyl-ethylene		—	—	40000	(.47)	I.C.T. Fig. 90

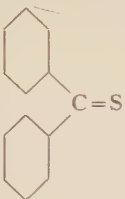
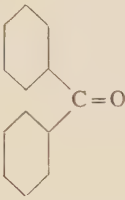
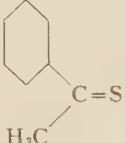
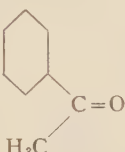
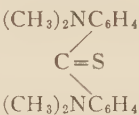
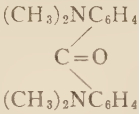
¹ L. Louis Light, Zeits. f. physik. Chemie **A122**, 414 (1926).
 B.H. J. Bielecki and V. Henri, Ber. d. D. Chem. Ges. **47**, 1690 (1914).
 Ley H. Ley, Ber. d. D. Chem. Ges. **51**, 1808 (1918).

I.C.T. International Critical Tables, Vol. 5.

² See note 3, Table I.

³ The terms (hex.) and (alc.) refer to absorption curves for the molecules in hexane or alcohol solution.

TABLE III. Absorption of compounds containing C=S groups.

MOLECULE	STRUCTURAL FORMULA	LONGEST λ REGION ¹ (IN CM ⁻¹)	REF. ²	NEXT ABS. REGION	REF. ²
Thiobenzophenone		16500 (blue) (di. ph. eth.)	B. Fig. 13	32000 (ether)	B. Fig. 9
Benzophenone		29500 (colorless) (di. ph. eth.)	B. Fig. 13 also II	39200 (hex.)	II also B. Fig. 17
Thioacetophenone		(blue violet)	B.	—	—
Acetophenone		31200 (alc.) (colorless)	II also B. Fig. 7	35900	II
Tetramethyl- diaminothiobenzophenone		17500 (eth.)	B. Fig. 12	22500 (meth. alc.)	B. Fig. 15
Tetramethyl- diaminobenzophenone		(weak yellow)	B.	27500 (meth. alc.)	B. Fig. 15

¹ The abbreviations, di. ph. eth., eth., alc., meth. alc., hex. refer, respectively, to the following solvents: diphenyl ether, ether, alcohol, methyl alcohol, and hexane.

² B. refers to Burawoy, reference 29, *I.C.T.*, to the *International Critical Tables*, and II, to Table II, references.

The phenones and styrene possess absorption regions of similar intensity near $\lambda 2800$. Since this region appears in styrene where no C=O group is present, the $\lambda 2800$ regions in these molecules must be due to the $N \rightarrow V_1$ transition.

V. ABSORPTION OF CONJUGATED THIO COMPOUNDS

In I it was pointed out that the C=S group has a similar electronic structure to the C=O

group and that the C=S absorption regions should be expected at longer wave-lengths than for that from C=O because the $3p_y$ electron of the sulfur atom is less firmly bound than the $2p_y$ oxygen electron to which it corresponds.

Burawoy²⁹ has studied the chromophoric power of various molecular groups and his data include information on several pairs of molecules

²⁹ A. Burawoy, *Ber. d. D. Chem. Ges.* **63**, 3155 (1930).

which are similar except for the presence of a C=O group on one member of the pair where a C=S group is attached to the other.

Table III lists some of these related compounds showing the positions of the longest wave-length C=S and C=O absorption regions. The intensities for any two related molecules are

of the same order of magnitude and the absorption from the C=S group is always at longer wave-lengths than that from the C=O group.

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